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Anisotropy of the linear and third-order nonlinear optical properties of a stretch-oriented polymer film of poly-[2, 5-dimethoxy paraphenylenevinylene]

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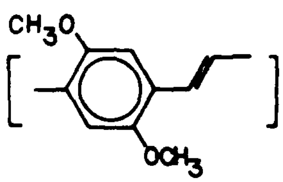
Large linear refractive index birefringence, strong dichroic behavior, and highly anisotropic $\chi^{(3)}$ have been observed for a uniaxially oriented poly (2, 5-dimethoxy paraphenylene vinylene) film. A subpicosecond time-resolved degenerate four-wave mixing study reveals an unusual behavior. Along the draw direction $\chi^{(3)}$ is complex with a negative real part and has a response time that is longer than the optical pulse resolution. In contrast, $\chi^{(3)}$ along the transverse direction is largely real and positive. Its response time is much faster, and is limited by the laser pulse width of ~400 fs.

Conjugated organic polymers are emerging as an important class of third-order nonlinear optical materials for photonics applications in the form of integrated optical devices. The origin of large third-order nonlinearity, $\chi^{(3)}$, lies in the extended π-conjugation effect which in nonresonant cases provides femtosecond response times.[1] In a recent study, we have shown that poly(paraphenylenevinylene) commonly abbreviated as PPV is a promising polymer because it has a relatively high $\chi^{(3)}$ value and can conveniently be processed into various shapes (such as planar waveguides) using a soluble precursor route.[2] Another advantage offered by this polymer is that it is possible to create a whole class of chemically derivatized polymeric structures. An interesting derivative is poly-(2, 5 dimethoxy paraphenylenevinylene) commonly abbreviated as dimethoxy PPV where electron donating methoxy groups have been substituted at the 2 and 5 position of the phenyl ring as shown below:



This increased electron density along the polymer chain reduces the band gap of the polymer and can be expected to enhance $\chi^{(3)}$. Furthermore, we have developed a special processing scheme by which we could make optical quality uniaxially stretch-oriented films to study the anisotropy of $\chi^{(3)}$. Device concepts such as polarization bistability have been proposed[3] which would utilize the anisotropy of $\chi^{(3)}$.

In this letter we report a very unusual anisotropic behavior in both the linear and nonlinear optical responses which, to our knowledge, has not been reported before. A large birefringence of linear refractive index, a strong dichroic behavior, and a large anisotropy of $\chi^{(3)}$ are found when comparing these properties along the draw direction and those in the transverse direction. Another unusual feature of $\chi^{(3)}$, deduced from a theoretical analysis of its observed polar plot, is that along the draw direction it appears to be predominantly complex with the real part having a negative sign and a response time longer than the pulse autocorrelation. In contrast, $\chi^{(3)}$ in the transverse direction appears to be mainly real with a positive sign and a response time limited by the resolution of our optical pulse.

In order to increase the solubility and improve the ease of processing, a synthetic methodology similar to that reported by Momii *et al.*[4] was used. The precursor polymer was soluble in chloroform and was cast, simultaneously stretch oriented/partially converted, and finally annealed to produce the dimethoxy PPV film. The stretch orientation and partial conversion of the precursor polymer were performed on an apparatus designed and built for this purpose at Foster-Miller.[5] A thin-film sample with a 6:1 uniaxial stretch orientation was mounted on a circular ring and placed on a scaled rotation stage. The film was rotated around the normal to the plane. The angle $\theta = 0$ refers to a situation when the draw direction (the director) is parallel to the electric field vector of the light ($\parallel$), whereas at $\theta = 90$ the electric field of light is transverse to the director ($\perp$).

The thickness of the film sample was measured with a Shieffield Universal Slide Spectre profilometer (RLU model 1) which yielded an average value of 1.45 ± 0.05 μm. Refractive indices for the principal axes in the film plane were evaluated using the method described by Swanepoel.[6] The transmission of *s*-polarized light was recorded as a function of wavelength within a range of 800–500 nm for both the normal incidence to the film and at a 30° incidence angle. The wavelengths at the corresponding extrema of interference fringes and previously measured thickness of the film were used to estimate an interference order number, which subsequently was used for calculations of the refractive index. The respective refractive indices thus derived are $n_{\parallel} = 3.1$ and $n_{\perp} = 1.78$, at $\lambda = 602$ nm.

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Degenerate four-wave mixing (DFWM) in a backward wave geometry was used to measure the magnitude and the time response of $\chi^{(3)}$. Since the film exhibits a remarkable birefringence, particular care was taken to ensure that the plane of the film was normal to the counterpropagating laser beams. Polarization of all beams was set parallel and vertical to the incidence plane. Only under such conditions does each beam have the s polarization and sees the same refractive index of the film. For a selected angular orientation θ and at a given power level (monitored by a reference photodiode), the backward beam delay was scanned to obtain the time response of the DFWM signal.

The laser system consists of a cw mode-locked Nd-YAG laser (Spectra–Physics model 3800), the pulses from which are compressed in a fiber optical pulse compressor and frequency doubled to pump a dye laser. The pulses are amplified in a three-state amplifier pumped with a pulsed Nd-YAG laser (Quanta Ray DCR-2A). In our study output pulse duration was ~400 fs with an average energy of 0.4 mJ, and a repetition rate of 30 Hz; the wavelength was 602 nm.

The stretched film of dimethoxy PPV is dichroic and strongly birefringent. Figure 1 is an illustration of both these effects. The absorption edge measured with light polarized parallel to the director is considerably red shifted when compared to the absorption edge observed with light polarized in the transverse direction. The absorption coefficients estimated at 602 nm are 4.4×10^3 and 1.9×10^2 cm^{-1} for parallel and transverse polarization, respectively. The fringe pattern in the long-wavelength region is distinctly more frequent in the parallel polarization than in the transverse polarization. This suggests a higher value for the refractive index in the parallel polarization. The calculated values of the refractive indices as discussed above are widely different for the two principal optical axes in the film plane: $n_\parallel = 3.1$ and $n_\perp = 1.78$, at 602 nm. Our Brewster angle measurement results on the same samples are also consistent with these refractive index values. This is an unusually large birefringence for a polymer.

The representative time-resolved DFWM signals for the two orthogonal directions in the dimethoxy PPV film are shown in Fig. 2. When all the beams are polarized parallel to the draw direction the DFWM signal reveals a slowly decaying component due to resonant excitation. In contrast, the decay of the DFWM signal in the transverse direction is extremely fast, limited by the laser pulse width. However, the magnitude of the DFWM signal is significantly reduced for the transverse direction. A power dependence study also indicates a decreasing effect of the resonant process in the transverse direction. The power dependence of the DFWM signal changes from an exponent of 2, for the parallel arrangement, to that of 2.4, in the transverse direction which is closer to the value of 3 expected for a truly nonresonant process.

The magnitude of $\chi^{(3)}$ for the dimethoxy PPV film was measured using CS_2 as a reference. The DFWM signal S was observed for the film and the reference sample under the same experimental conditions. The $\chi^{(3)}$ value for the film was calculated using the following formula:

$$|\chi^{(3)}| = (n/n_r)^2(l_r/l)(S/S_r)^{1/2}A\,|\chi_r^{(3)}|, \tag{1}$$

where $A = \ln(t)/(1-t)\sqrt{t}$ is the absorption correction factor for the film; t is the optical transmission of the film. Parameters with subscript r refer to the reference substance CS_2; $n_r = 1.626$, $\chi_r^{(3)} = 6.8\times10^{-13}$ esu. We find $\chi_\parallel^{(3)} = (4\pm1)\times10^{-9}$ esu, with $n_\parallel = 3.1$, $A = 3.99$, and measured thickness $l = 1.45\ \mu$m. This is a very high value of $\chi^{(3)}$ and is much higher than the corresponding value for a similarly stretch-oriented PPV film.[7] For the analysis of the $\chi^{(3)}$ anisotropy measurements, Eq. (1) can be rearranged into another form, including reflection losses R, at the film surfaces to yield

$$|\chi_\theta^{(3)}|^2 = (n_\theta/n_0)^4(A_\theta/A_0)^2 \times[(1-R_0)^2/(1-R_\theta)^2](S_\theta/S_0)|\chi_0^{(3)}|^2. \tag{2}$$

In the above equation, the parameters with a subscript θ refer to the values at a given rotation angle θ which the draw direction makes with the polarization (vertical) of the laser beams. The parameters with subscripts 0 refer to $\theta = 0$. Experimental measurement of the reflection loss indicated that this effect was not sensitive to the rotation angle θ. Calculations of the anisotropic reflectivity for a given set of refractive indices and absorption coefficients also confirmed this

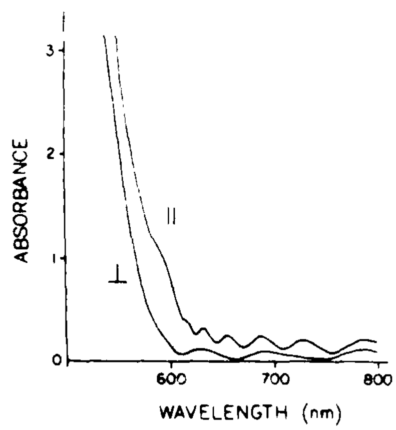

FIG. 1. Absorption spectra of the 6:1 stretch oriented 2, 5-dimethoxy PPV film with two different polarizations: || refers to the polarization parallel to the draw direction, ⊥ refers to the polarization in the transverse direction.

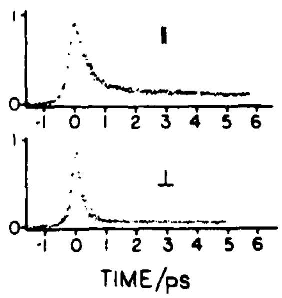

FIG. 2. Degenerate four-wave mixing signal as a function of time delay of the backward wave beam; || and ⊥ represent the results when the polarization of all the beams is parallel and transverse, respectively, to the draw direction.

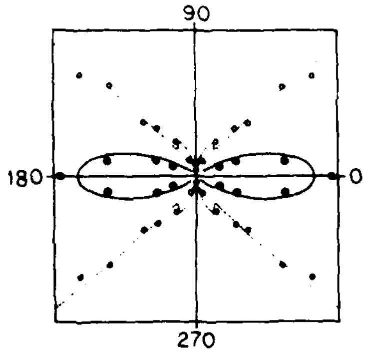

FIG. 3. Polar plot (orientational anisotropy) of the $|\chi^{(3)}|^2$. The solid circles represent the data points; the hollow circles represent the data points on 30 times expanded scale. The solid and dotted lines are corresponding theoretical fits.

conclusion But the dependence of n and A on θ was significant.

Knowing the values of the macroscopic refractive indices for principal directions in the film plane, the refractive index $n(\theta)$ can be calculated from the indicatrix equation. The effective transmission of the film was measured at wavelength $\lambda = 602$ nm, from $\theta = 0°$ to $90°$ at intervals equal to $10°$ which yielded information on $A(\theta)$. Then using Eq. (2) $|\chi_\theta^{(3)}|^2$ was obtained as a function of θ. The results are shown as the full circles and open circles in Fig. 3. The open circles represent the $|\chi_\theta^{(3)}|^2$ values multiplied by a constant in order to be shown on a magnified scale. The $|\chi^{(3)}|$ value shows a large anisotropy with $|\chi_\parallel^{(3)}|/|\chi_\perp^{(3)}| = 24.9$.

To explain the experimentally determined polar plot we use a phenomenological description of anisotropy of macroscopic $\chi^{(3)}$. Assuming an orthorhombic symmetry for a *uniaxially stretched film, we start from the following expression* which we have successfully used for nonresonant cases[7,8]:

$$\chi_\theta^{(3)} = \chi_\parallel^{(3)} \cos^4\theta + \chi_{\rm off}^{(3)} \sin^2\theta \cos^2\theta + \chi_\perp^{(3)} \sin^4\theta. \quad (3)$$

Here $\chi_{\rm off}^{(3)}$ represents an in-plane, off-diagonal component of the $\chi^{(3)}$ tensor. For the dimethoxy PPV film we should, however, consider both the real and the imaginary components of a complex third-order susceptibility, i.e., $\chi_\theta^{(3)} = \chi_\theta'^{(3)} + i\,\chi_\theta''^{(3)}$, which yields two equations similar to Eq. (3) to describe both the real and the imaginary parts. As discussed above the DFWM study yields $|\chi^{(3)}|^2$ which can be expressed in the reduced form

$$\frac{|\chi_\theta^{(3)}|^2}{|\chi_0^{(3)}|^2} = \frac{(\chi_\theta'^{(3)})^2 + (\chi_\theta''^{(3)})^2}{(\chi_0'^{(3)})^2 + (\chi_\theta''^{(3)})^2} = (\chi_\theta'^{(3)})^2 + (\chi_\theta''^{(3)})^2, \quad (4)$$

which has been normalized by taking $(\chi_\theta'^{(3)})^2 + (\chi_0''^{(3)})^2 = 1$. Using a set of two equations like Eq. (3) for $\chi_\theta'^{(3)}$ and $\chi_\theta''^{(3)}$, which require five independent parameters to fit, the sum shown on the right-hand side of Eq. (4) was calculated for all angles θ, for which measurements were performed. The best-fit results are shown in Fig. 3 as the continuous and the dotted lines, which correspond to data represented by the full circles and the open circles, respectively. An important result is that a great improvement in the fit was achieved when we used opposite signs for the real part of $\chi^{(3)}$ for the parallel and transverse directions. For the transverse direction, the imaginary part of $\chi^{(3)}$ was found to be insignificant.

The complex parallel and transverse components of the $\chi^{(3)}$ tensor, found *in the process of data fitting, are as follows:* $\chi_\parallel^{(3)} = -0.83 + i\,0.56$, $\chi_\perp^{(3)} = 0.041$ and the off-diagonal term $\chi_{\rm off}^{(3)} = 0.57$. The inference of $\mathrm{Re}\,\chi_\parallel^{(3)} < 0$ and $\mathrm{Im}\,\chi_\parallel^{(3)} \gg \mathrm{Im}\,\chi_\perp^{(3)}$ is consistent with a highly resonant nature of optical nonlinearity for the draw direction.

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